**Pra titi n r' Dock t N .** 2002-IP-008949U1 **PATENT**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of: Michael A. McCabe, et al
Application No.: / Unknown Group No.: Unknown
Filed: Concurrently Herewith Examiner: Unknown
For: Liquid Gelling Agent Concnentrates and Methods of Treating Wells Therewith

**Commissioner for Patents**
**P.O. Box 1450**
**Alexandria, VA 22313-1450**

## EXPRESS MAIL CERTIFICATE

"Express Mail" label number ER276299069US

Date of Deposit 10-21-2003

I hereby state that the following *attached* paper or fee

Specification with 22 pages
Information Disclosure Statement with PTO-1449
Declaration
Power of Attorney
Statement Under 37 CFR 3.73(b)
Assignment with Recordation Sheet
Fee Transmittal
Patent Application Transmittal
Return Postcard

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. § 1.10, on the date indicated above and is addressed to the Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450

Tammy Knight
Typed or printed name of person mailing paper or fee

Tammy Knight
**Signature of person mailing paper or fee**

*NOTE: The label number need not be placed on each page. It should, however, be placed on the first page of each separate document, such as, a new application, amendment, assignment, and transmittal l tter for a fee, along with the certificate of mailing by "Express Mail." Although the label number may be on checks, such a practice is not required. In order not to deface formal drawings it is sugg sted that th label number be placed on the back of ach formal drawing or the drawings be accompanied by a set of informal drawings on which th label number is placed.*

# LIQUID GELLING AGENT CONCENTRATES AND METHODS OF TREATING WELLS THEREWITH

## BACKGROUND OF THE INVENTION

### 1. FIELD OF THE INVENTION

**[0001]** The present invention relates to liquid gelling agent concentrates and methods of treating wells using the concentrates.

### 2. DESCRIPTION OF THE PRIOR ART

**[0002]** Viscous gelled aqueous treating fluids are used in a variety of treatments in oil and gas wells including well completions and production stimulation treatments. An example of a well completion treatment which utilizes a viscous gelled aqueous fluid is known in the art as gravel packing. In gravel packing treatments, solid gravel particles such as sand are carried by way of the well bore to a subterranean zone in which a gravel pack is to be placed by a viscous gelled aqueous carrier fluid. That is, particulate solids (referred to in the art as gravel) are suspended in the viscous gelled aqueous carrier fluid at the surface and are carried to the subterranean zone in which the gravel pack is to be placed. Once the gravel is placed in the zone, the viscous gelled aqueous carrier fluid is broken (the viscosity is reduced) and recovered (returned to the surface) by a delayed viscosity breaker in the carrier fluid. The gravel pack produced functions as a filter to separate formation solids from produced fluids while permitting the produced fluids to

flow into and through the well bore.

[0003] An example of a production stimulation treatment utilizing a viscous gelled aqueous fluid is hydraulic fracturing. In hydraulic fracturing, a viscous gelled aqueous fluid, referred to in the art as a fracturing fluid, is pumped through the well bore into a subterranean zone to be stimulated at a rate and pressure such that fractures are formed and extended into the subterranean zone. The fracturing fluid also carries particulate solids, referred to in the art as proppant particles into the fractures. The proppant particles are suspended in the viscous gelled aqueous fracturing fluid so that the proppant particles are carried into the fractures. The viscous fracturing fluid is then broken by a delayed viscosity breaker in the fracturing fluid so that the proppant particles are deposited in the fractures and the fracturing fluid is removed from the subterranean zone. The proppant particles function to prevent the fractures from closing whereby conductive channels are formed through which produced fluids can flow to the well bore.

[0004] The viscous gelled aqueous treating fluids used in gravel packing, fracturing and other well procedures have heretofore been prepared by dissolving a dry powdered gelling agent into the vortex of a vigorously stirred aqueous fluid. This procedure has very often resulted in undesirable agglomerations of the gelling agent in the polymer which are called "fish eyes." Fish eyes are polymer masses wetted on the outside but with dry, unhydrated material inside. While mechanical gelling agent feeders and adductors have been utilized to more efficiently wet the gelling agent, the feeders and adductors often fail to prevent the formation of fish eyes.

[0005] More recently, storable liquid gelling agent concentrates have been developed and used. One such liquid gelling agent concentrate which has been used successfully comprised of particulate gelling agent which is suspended in a diesel oil carrier liquid. The particulate gelling agent is rendered suspendible in the hydrocarbon carrier liquid by a coating of a suspending agent and a surfactant on the particulate gelling agent. The particulate gelling agent is then dispersed in diesel oil or other hydrocarbon liquid to form the liquid gel concentrate. The liquid gel concentrate can be stored at the well site, and when a gelled aqueous treating fluid is required, the liquid gelled concentrate is readily combined with an aqueous fluid without the formation of fish eyes or other similar problems.

[0006] A problem with the liquid gelling agent concentrates utilized heretofore which include a hydrocarbon carrier fluid such as diesel oil is that the hydrocarbon carrier fluid contains compounds such as benzene, ethylbenzene, toluene, xylene and/or other compounds which are prohibited by the Environmental Protection Agency primary drinking water standards, i.e, Section 1429 of the Safe Drinking Water Act. Another problem with such gelling agent concentrates is that they can not be stored for long periods of time and they often do not have good pour abilities or non-settling properties. Thus, there are needs for improved storable liquid gel concentrates which are environmentally safe and meet the standards of the Safe Drinking Water Act and have long term storage, good pour abilities and non-settling properties.

## SUMMARY OF THE INVENTION

**[0007]** The present invention provides storable liquid gelling agent concentrates that have improved storage, pour abilities and settling properties and methods of treating wells using the concentrates. A liquid gelling agent concentrate of this invention basically comprises an environmentally safe hydrocarbon carrier liquid, an organophillic clay suspending agent, a surfactant for dispersing the organophillic clay suspending agent in the hydrocarbon carrier liquid, and a particulate aqueous fluid gelling agent suspended in the carrier liquid.

**[0008]** A method of this invention for treating a subterranean zone penetrated by a well bore using a viscous aqueous treating fluid is comprised of the following steps. A liquid gelling agent concentrate is mixed with an aqueous fluid to thereby form a viscous aqueous treating fluid. The liquid gelling agent concentrate comprises an environmentally safe hydrocarbon carrier liquid, an organophillic clay suspending agent, a surfactant for dispersing the organophillic clay suspending agent in the carrier liquid, and a particulate aqueous fluid gelling agent suspended in the carrier liquid. The viscous aqueous treating fluid is introduced into a subterranean zone to be treated.

**[0009]** The liquid gelling agent concentrate of this invention can be utilized in a variety of subterranean zone treatments such as fracturing subterranean zones, placing gravel packs in subterranean zones, and the like. The hydrocarbon carrier of the liquid gelling agent concentrate is an environmentally safe hydrocarbon liquid that meets the standards set forth in the Safe Drinking Water Act and does not include hazardous chemicals such

as benzene, ethylbenzene, toluene or xylene. The hydrocarbon carrier liquid utilized in the liquid gelling agent concentrate can carry up to five pounds of gelling agent per gallon of the concentrate. The liquid gelling agent concentrate has a high flash point and a low pour point. In addition, the liquid gelling agent concentrate can be stored for long periods of time, has good pour abilities and settling properties and is easily combined with water to form a viscous gelled aqueous treating fluid.

[0010] The objects, features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of preferred embodiments which follows.

## DESCRIPTION OF PREFERRED EMBODIMENTS

[0011] The present invention provides improved liquid gelling agent concentrates and methods of treating wells using the concentrates. The liquid gelling agent concentrates comprise an environmentally safe hydrocarbon carrier liquid, an organophillic clay suspending agent, a surfactant for dispersing the organophillic clay suspending agent in the carrier liquid, and a particulate aqueous fluid gelling agent suspended in the carrier liquid. The liquid gelling agent concentrates can be stored for long periods of time and they have good pour abilities and non-settling properties.

[0012] The methods of this invention for treating a subterranean zone penetrated by a well bore using a viscous aqueous treating fluid comprises the following steps. A liquid gelling agent concentrate of this invention is mixed with an aqueous fluid to thereby form a viscous aqueous treating fluid. Thereafter, the viscous aqueous treating fluid is

introduced into the subterranean zone.

[0013] An example of an environmentally safe hydrocarbon carrier liquid that can be utilized in accordance with this invention is a mixture of hydrocarbons having in the range of from about 6 to about 13 carbon atoms obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst. This mixture of hydrocarbons is commercially available under the trade designation "ENVIRONDRILL™" from Wells Cargo Oilfield Services of Calgary, Alberta, Canada. Another example is a mixture of hydrocarbons having in the range of from about 10 to about 25 carbon atoms obtained by catalytic hydrogenation of vacuum gas oils followed with dewaxing by hydroisomerization and stabilization by hydrotreating at high pressures. This mixture of hydrocarbons is commercially available under the trade name "PURE DRILL IA-35™" which is commercially available from Petro-Canada of Mississauga, Ontario, Canada. Yet another example is a mixture of severely hydrocracked low toxicity mineral oils and synthetic isoalkanes. This hydrocarbon mixture is commercially available under the trade designation "PURE DRILL HT-40™" from Petro-Canada of Mississauga, Ontario, Canada.

[0014] Other environmentally safe hydrocarbons that can be utilized as carrier liquids in accordance with this invention include, but are not limited to, mixtures of linear alpha and internal olefins; polyalpha olefins; mixtures of $C_{10}$-$C_{14}$ alkanes and $C_8$ and higher alkenes; mixtures of linear alpha and internal olefins; hydrocarbon blends containing 93% linear paraffins; blends of isoalkanes, isoalkenes and alcohols; blends of linear internal olefins having from about 16 to about 18 carbon atoms; blends of linear alpha-

olefins having 10 or more carbon atoms; vegetable oils; and vegetable esters.

[0015] Of the foregoing environmentally safe hydrocarbon carrier liquids, a mixture of hydrocarbons having in the range of from about 6 to about 13 carbon atoms obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst is preferred. This carrier liquid has a flash point above about 175°F and a pour point below about -49° F.

[0016] The hydrocarbon carrier liquid utilized is generally present in the liquid gelling agent concentrate in an amount in the range of from about 25% to about 55% by weight of the concentrate.

[0017] A variety of organophillic clay suspending agents can be utilized in the liquid gelling agent concentrate. Generally, organophillic clays which are formed by reacting quaternary ammonium salts with water swellable clays are preferred. The quaternary ammonium salts utilized are preferably those wherein the quaternary ammonium substituents are alkyl radicals, two of which have in the range of from 1 to 10 carbon atoms and the other two having in the range of from 10 to 30 carbon atoms. The most preferred organophillic clays for use in accordance with the present invention include, but are not limited to, quaternary ammonium bentonite clay, quaternary ammonium montmorillinite clay and quaternary ammonium hectorite clay. Of these, quaternary ammonium bentonite clay is the most preferred. The organophillic clay utilized is included in the liquid gelling agent concentrate in an amount in the range of from about 0.2% to about 4% by weight of the concentrate.

[0018] Examples of surfactants that can be used for dispersing the organophillic clay suspending agent in the carrier liquid include amphoteric surfactants, anionic surfactants, cationic surfactants and nonionic surfactants. Examples of specific such surfactants include, but are not limited to, nonionic esters, polyethylene glycol esters, ethoxylated acids, ethoxylated oils, sorbitol esters, ethoxylated sorbitol esters, ethoxylated alcohols, alcohol alkoxylates, alkanolamides, quaternary ammonium compounds, dialkyl quaternary ammonium compounds, benzyl quaternary ammonium compounds, amine oxides, ethoxylated amines, fatty imidazolines, ether carboxylates, sulfonates, sulfosuccinates, fatty acid taurates, ether carboxylates, alkyl betaines, and alkyl amidopropyl betaines. Of the foregoing surfactants, ethoxylated alcohol is generally preferred. The surfactant utilized is included in the liquid gelling agent concentrate in an amount in the range of from about 0.1% to about 2% by weight of the concentrate.

[0019] Any of a variety of particulate gelling agents can be utilized in accordance with the present invention. The gelling agents generally include a water dispersable or water soluable hydrophilic colloid such as cellulose derivatives, starch derivatives, gums including ghatti, Arabic, tragacanth, locust bean, karaya, carrageenan, algin, and derivatives of such gums, biopolymers and mixtures thereof. Examples of preferred particulate aqueous fluid gelling agents for use in accordance with the present invention include, but are not limited to, guar, hydroxypropylguar, carboxymethylhydroxyproplyguar, hydroxyethylcellulose, carboxymethylhydroxyethylcellulose, carboxymethylceullose, xanthan and succinoglycan. Of these, guar is the most preferred. The particulate aqueous fluid gelling agent utilized is generally present in the liquid gelling agent concentrate in an

amount in the range of from about 25% to about 55% by weight of the concentrate, i.e., up to and including 5 pounds of gelling agent per gallon of the concentrate.

[0020] As mentioned, the liquid gelling agent concentrates of this invention preferably include environmentally safe hydrocarbon carrier liquids that meet the standards set forth in the Environmental Protection Agency Safe Drinking Water Act. As also mentioned, the liquid gelling agent concentrates can contain particulate aqueous fluid gelling agents in amounts up to five pounds of particulate aqueous fluid gelling agent per gallon of the concentrates and higher. Also, the preferred liquid gelling agent concentrates of this invention have higher flash points than the heretofore utilized liquid gel concentrates, i.e., flash points as high as 175°F and pour points that are lower than the heretofore used concentrates, i.e., -49°F and lower.

[0021] The liquid gelling agent concentrates of this invention have long term storage, good pour abilities and non-settling properties. For example, the preferred liquid gelling agent concentrates of this invention can be stored for seven days at 80°F without significant settling of the particulate gelling agent therein and less than 2% free liquid.

[0022] A preferred liquid gelling agent concentrate of this invention comprises: an environmentally safe hydrocarbon carrier liquid; an organophillic clay suspending agent; a surfactant for dispersing the organophillic clay suspending agent in the carrier liquid; and a particulate aqueous fluid gelling agent suspended in the carrier liquid.

[0023] Another preferred liquid gelling agent concentrate comprises: an environmentally safe hydrocarbon carrier liquid comprising a mixture of hydrocarbons having in the

range of from about 6 to about 13 carbon atoms obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst present in an amount in the range of from about 25% to about 55% by weight of the concentrate; a quaternary ammonium bentonite clay suspending agent present in an amount in the range of from about 0.2% to about 4% by weight of the concentrate; an ethoxylated alcohol surfactant present in an amount in the range of from 0.1% to about 2% by weight of the concentrate; and a guar particulate aqueous fluid gelling agent present in an amount in the range of from about 25% to about 55% by weight of the concentrate.

**[0024]** A preferred method of this invention for treating a subterranean zone penetrated by a well bore using a viscous aqueous treating fluid comprises the steps of: (a) mixing a liquid gelling agent concentrate with an aqueous fluid to thereby form a viscous aqueous gelled treating fluid, the liquid gelling agent concentrate comprising an environmentally safe hydrocarbon carrier liquid, an organophillic clay suspending agent, a surfactant for dispersing the organophillic clay suspending agent in the carrier liquid, and a particulate aqueous fluid gelling agent suspended in the carrier liquid; and (b) introducing the viscous aqueous gelled treating fluid into the subterranean zone.

**[0025]** Another preferred method of treating a subterranean zone penetrated by a well bore using a viscous aqueous treating fluid comprises the steps of: (a) mixing a liquid gelling agent concentrate with an aqueous fluid to thereby form a viscous gelled aqueous treating fluid, the liquid gelling agent concentrate comprising an environmentally safe hydrocarbon carrier liquid that comprises a mixture of hydrocarbons having in the range of from about 6 to about 13 carbon atoms obtained by treating a petroleum fraction with

hydrogen in the presence of a catalyst present in an amount in the range of from about 25% to about 55% by weight of the concentrate, a quaternary ammonium bentonite clay suspending agent present in an amount in the range of from about 0.2% to about 4% by weight of the concentrate, an ethoxylated alcohol surfactant present in an amount in the range of from about 0.1% to about 2% by weight of the concentrate, and a guar particulate aqueous fluid gelling agent present in an amount in the range of from about 25% to about 55% by weight of the concentrate; and (b) introducing the viscous aqueous treating fluid into the subterranean zone.

**[0026]** In order to further illustrate the liquid gelling agent concentrate and methods of this invention, the following examples are given.

EXAMPLE 1

**[0027]** A liquid gelling agent concentrate of this invention (referred to herein as "Inventive Concentrate") was prepared in the laboratory comprising 43% by weight of diesel oil, 1% by weight of a quaternary ammonium bentonite clay suspending agent, 1% by weight of an ethoxylated alcohol surfactant for dispersing the suspending agent, and a 55% by weight of a guar particulate gelling agent.

**[0028]** A prior art gelling agent concentrate (referred to herein as "Concentrate A") published by Union Carbide Corporation was also prepared comprising 53.83% by weight diesel oil, 1.39% by weight organophillic clay, 0.28% by weight methanol, 42.5% by weight hydroxyethylcellulose and 2.0% nonylphenol surfactant.

[0029] Each of the above described liquid gelling agent concentrates was placed in an 80°F water bath and after time intervals of 24 hours, 48 hours, 72 hours and 168 hours, the percent of free liquid separation and the settling of solids in the concentrates were observed.

[0030] The results of these tests are given in Tables I and II below.

TABLE I

| % Free Liquid Separation | | | | |
|---|---|---|---|---|
| Concentrate | 24 hours at 80°F | 48 hours at 80°F | 72 hours at 80°F | 168 hours (7 days) at 80°F |
| Inventive Concentrate | 0 | 0 | 0 | 1.4 |
| Concentrate A | 2.1 | 2.3 | 2.4 | 2.4 |

TABLE II

| Settling of Solids | | | | |
|---|---|---|---|---|
| Concentrate | 24 hours at 80°F | 48 hours at 80°F | 72 hours at 80°F | 168 hours (7 days) at 80°F |
| Inventive Concentrate | 0 | 0 | 0 | 0 |
| Concentrate A | 0 | trace | Ring[1] | Ring[1] |

[1] Ring means the presence of solids in the bottom of the container forming a ring.

[0031] From Tables I and II, it can be seen that the Inventive Concentrate can be stored for at least seven days at 80°F without settling and with less than 2% free liquid.

EXAMPLE 2

[0032] Samples of the Inventive Concentrate and Concentrate A described in Example 1 as well as two other prior art concentrates designated "Concentrate B" and "Concentrate

C" were tested for viscosity using a Brookfield viscometer equipped with a number 3 spindle at 20 rpm and at a temperature of 80°F.

[0033] Concentrate B was prepared comprising 49% by weight of diesel oil, 5% by weight of an aqueous emulsion of a suspending agent comprising water insoluble polymer particles that swell when contacted with diesel oil and 46% by weight of polysaccharide water soluble gelling agent. This concentrate is described in detail in U.S. Patent No. 4,772,646 issued to Harms, et al. on September 20, 1988 which is incorporated herein by reference thereto.

[0034] Concentrate C published by Hercules, Inc. was prepared comprising 37% by weight of hydroxyethylcellulose, 40.1% by weight of an ethyl hexanol premix containing 1% hydroxypropylcellulose, 21.1% by weight of mineral oil and 1.8% by weight of an ethoxylated alcohol surfactant.

[0035] The results of these tests are given in Table III below.

TABLE III

| Samples Tested | Viscosity, cP | | | |
|---|---|---|---|---|
| | Concentrate A | Concentrate B | Concentrate C | Inventive Concentrate |
| 1 | 960 | 3008 | 3904 | 650 |
| 2 | 512 | 4736 | 4352 | 780 |
| 3 | 1088 | 4608 | 4928 | 850 |
| 4 | -- | -- | 5632 | 860 |
| 5 | -- | -- | 4736 | 852 |

[0036] From Table III, it can be seen that the Inventive Concentrate has the lowest

viscosity which provides excellent pour ability.

[0037] Thus, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those which are inheritant therein. While numerous changes can be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.

[0038] What is claimed is: